

Photodissociation of F₂ in crystalline krypton: effect of molecule–lattice prealignment

H. Kunttu and V.A. Apkarian

Institute for Surface and Interface Science, Department of Chemistry, University of California, Irvine, CA 92717, USA

Received 20 April 1990; in final form 1 June 1990

Photodissociation studies of F₂ isolated in crystalline krypton are reported. At an excess energy of 1.16 eV, the dissociation quantum yield is 12%. The quantum yield reaches unity for excess energies above 2.5 eV. At 4 K, dissociation probabilities are higher than at 12 K. This inverse temperature dependence is ascribed to prealignment of the molecule along a reaction cone of the cage.

1. Introduction

Oriental effects can be expected to play a significant role in reactive dynamics in crystalline media. Prealignment of reagents by the lattice, or guiding of reagents through preferred directions in the ordered lattice are possible sources of such effects. As a prototype of solid state reactions, we consider the photodissociation of small molecules isolated in a crystalline lattice. In such a process, we may suspect that the relative molecule–lattice prealignment would influence the outcome of the event, i.e. the cage exit probabilities of fragments. While such expectations seem natural, to our knowledge, there have not been any clear demonstrations of such effects. In this communication we report on photodissociation studies of F₂ in crystalline Kr, in which the expected effect of molecule–lattice prealignment on cage exit probabilities is thought to be observed. Since the observations are indirect, they are extracted from temperature dependence of dissociation quantum yields, the interpretations rely heavily on prior theoretical simulations.

Photodissociation of F₂ in crystalline argon was recently studied experimentally [1,2], and was compared to theoretical molecular dynamics (MD) simulations [3] of the same system. As a first example of solid state reactive dynamics studies in which direct comparisons between theory and experiment and

afforded, the extent of agreement has been satisfying. Among the main conclusions of the MD simulations that have been verified experimentally are:

(i) Photodissociation of F₂ is subject to only a minor cage effect leading to 100% cage exit probability at excess energies above 2.5 eV – a result that should be put in the context of prior studies of similar systems, e.g. the photodissociation of Cl₂ and ICl in rare gas matrices [4,5] show quantum yields less than 10⁻⁶.

(ii) Upon the initial impulse, F atoms undergo long range migration in the lattice, in an almost guided motion. This has been indirectly verified, through observations of long range photomobility of F atoms in solid Ar [2], and Xe doped Ar [1,6].

(iii) Product F atoms occupy interstitial O_h sites in the lattice, as verified experimentally in solid Ar multiply doped with F and Kr [1].

The experimental verification of these predictions give credibility to the detailed picture of dissociation dynamics derived from the MD simulations. Namely, the cage of exit of F atoms is impulsive in nature, happening through well defined “windows”, rather than involving multiple collisions with the surrounding cage. This is in contrast with the picture derived for HI dissociation in Xe, in which delayed cage exit of the H fragment is observed in the MD simulations [7]. We note, however, that in recent experimental measurements of a related system, H₂O/D₂O dis-

sociation in Ar and Kr, no evidence of delayed cage exit has been found [8].

Dissociation through reaction windows, or cones, leads immediately to the consideration that, at least for low excess energies, the molecule–lattice relative orientation should play a role in the probability of cage exit. A clear signature of this effect in the MD simulations of F_2/Ar , was the observation of an inverse temperature dependence of dissociation quantum yields – at 4 K the cage exit probability was predicted to be higher than at 12 K [3]. This prediction is specific to F_2/Ar . In the related system of Cl_2 photodissociation in Xe, the MD simulations predict impulsive dissociation at elevated temperatures [9]. Although the temperature dependence is not predicted to be monotonic in that case, the overall trend is an increase in cage exit probabilities with increasing temperature. The contrast between these two systems is explained by the molecule–cage relative motions. In the case of F_2 , the molecule occupies a loose-fit substitutional site; and at 12 K, executes what may be referred to as a rotation–translation coupled motion [10]. At 4 K, F_2 freezes in a librational well, pointing at one of the cones of reaction. Thus, upon warm-up, the rotating molecule increasingly samples the nonreactive orientations. In the case of Cl_2 , the molecule occupies a tight-fit substitutional site, locked into a nonreactive orientation. As a result, the photodissociation threshold is observed to coincide with the onset to free rotation. These theoretical predictions, had to data, not been verified experimentally.

Despite the fairly good agreement between experiment and theory in the previous studies of F_2/Ar , rather large error bars in the experimental data made the comparisons only semi-quantitative [2]. Although, an attempt was made to test the theoretically predicted temperature effect, due mainly to experimental difficulties, no conclusions could be drawn. The experimental difficulties in the F_2/Ar system can mostly be related to the rather unstable probe laser (ArF excimer laser at 193 nm), and the fact that the probe also induced photomobility and subsequent recombination of the fragments. We have therefore resorted to studies of F_2 dissociation in crystalline krypton, in which these experimental difficulties are absent. Moreover, we suspected that the inverse temperature dependence could be even more pro-

nounced in Kr than in Ar. Two considerations lead to this expectation: (a) the F–Kr and F–Ar potentials are nearly identical near the bottom of their van der Waals pair potentials [11]; (b) given the larger substitutional cavity in Kr, the motion of F_2 should be even better described by the rotation–translation coupling model and reactive cones with larger acceptance angles should control the cage exit dynamics. This expectation has been realized experimentally.

2. Experimental

The experiments, were conducted in $1\text{ cm} \times 1\text{ cm} \times 1\text{ cm}$ free standing crystals, which were transparent to the naked eye. The crystal preparation methods have been described elsewhere [1]. We rely on methodologies largely developed by Schwentner and coworkers [12]. The F_2 concentration was kept low, 1:10000 to 1:30000, in order to obtain optically nonscattering crystals. A closed-cycle refrigerator (Air Products Displex, DE-202) was used for the 12 K measurements. A He flow cryostat (Air Products Heli-Tran) was used for the temperature dependence measurements between 4 and 12 K. Krypton of 99.999% purity (Spectra Gases) and fluorine of 97% purity (Matheson) were used without further purification.

The photodissociation of F_2 is followed by monitoring the production of F atoms. This is accomplished by monitoring the $Kr_2^+ F^-$ exciplexic emission, upon optically accessing the F–Kr charge transfer states. An energy level diagram illustrating this scheme is shown in fig. 1. The technique is rather general, and can be applied as a sensitive laser-induced fluorescence scheme for the detection of halogen atoms in the presence of rare gases – be it in the gas, liquid, or solid phases [13,14]. The charge transfer states of F in solid Kr have previously been described in some detail [1]. The main excitation, near 275 nm, is ascribed to a state delocalized among immediate nearest neighbors, assigned to $Kr_6^+ F^-$. The main emission, is a broad band from the localized triatomic exciplex, $Kr_2^+ F^-$, centered near 450 nm. In the present, the photodissociation and F atom probe photodynamics can be illustrated as

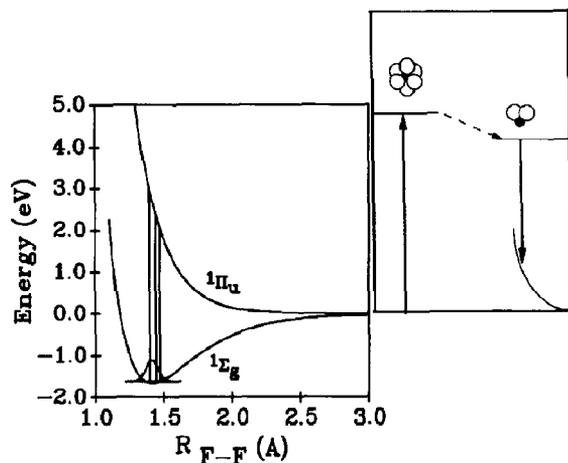
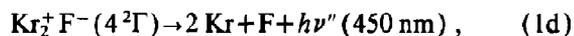
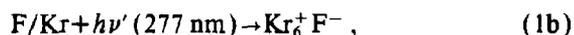
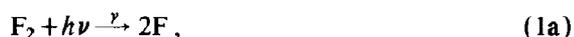


Fig. 1. Energetics of F_2 photodissociation, and F atom probe in crystalline krypton. In the left panel the gas phase, bound and dissociative surfaces of F_2 are shown. The schematic in the right panel illustrates the laser-induced fluorescence technique for following F atom production in the solid. F atoms in the solid are interrogated by exciting the Kr-F charge transfer excitation near 4.5 eV. The positive charge in this state is delocalized over immediate nearest neighbors, hence more appropriately described as $Kr_6^+ F^-$. This vertically accessed state localizes to the triatomic exciplex configuration, $Kr_2^+ F^-$, on a time scale less than 1 ps. The latter state relaxes radiatively with a broad bound-repulsive emission centered near 450 nm.



where $h\nu$ is the dissociating pulse, $h\nu'$ the probe and $h\nu''$ the exciplex emission. Thus, the 450 nm emission induced by a weak probe near 275 nm, is directly proportional to the F atom concentration in the solid. When F_2 is irradiated, the exciplex emission intensity, E (at 450 nm), grows exponentially

$$E(t) = E_\infty [1 - \exp(-\gamma I t)], \quad (2)$$

in which I is the fluence of the dissociating laser; γ represents the photodissociation cross section: $\gamma = \Phi\sigma$, is the product of dissociation quantum yield (Φ) and the absorption cross section (σ) of F_2 at a given wavelength. An example of a growth curve and its fit to an exponential is shown in fig. 2. The dissociation

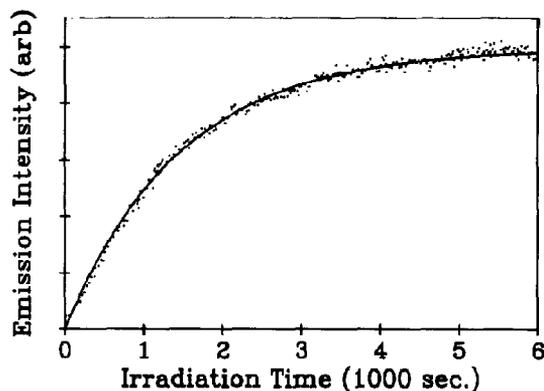


Fig. 2. A typical growth curve, 450 nm emission versus irradiation time, is shown. The example is from an $F_2:Kr$, 1:10000 sample. Both photodissociation and probe are carried out at the same wavelength, 277 nm, in this case. The photodissociation is carried out with 2.5 mJ cm^{-2} at a laser repetition rate of 10 Hz.

can be carried out to completion, as evidenced from the well defined plateau reached, and independently verified by transmission measurements [1,2]. γ is directly obtained from the fit. The quantum yield for dissociation at different wavelengths is then extracted by using the gas phase absorption cross sections [15]. Based on our previous finding, that the absorption lineshape and strength of F_2 in liquid Ar is within experimental error identical to that in the gas phase [2], no dielectric corrections are made for absorptions cross sections.

The growth curves were recorded by overlapping the dissociating beam and the probe beam within the entire length of the crystal. To avoid dissociation by the probe, a weak beam $\approx 1 \mu\text{J/pulse}$, at 277 nm is used. As dissociation source, either the fundamental, or the frequency doubled output of a dye laser was used with typical intensities of 80 mJ cm^{-2} . However, for measurements at 280 nm, the laser intensity was reduced to 2.5 mJ cm^{-2} to avoid the previously reported two-photon-induced charge transfer dissociation of F_2 in Kr [1].

3. Results and discussion

Quantum yields as a function of photodissociation excess energy are listed in table 1, and presented in the bar-graph of fig. 3. Excess energy, is defined as the energy above the gas phase dissociation limit of

Table 1
Photodissociation quantum yield for molecular fluorine in crystalline Kr at different excitation energies

λ (nm)	E_{excess} (eV)	Φ (%)	
		12 K	4.5 K
450	1.1	12	35
390	1.6	38	75
340	2.0	89	
308	2.4	97	
280	2.8	100	

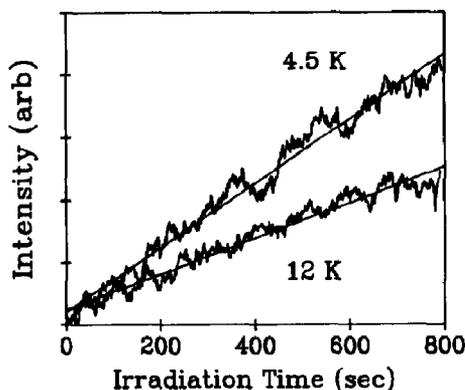


Fig. 3. Top panel: experimental photodissociation quantum yields of F_2 in crystalline Kr. Bottom panel: theoretical quantum yields for the dissociation of F_2 in solid Ar (see ref. [3]).

$F_2: E_{\text{excess}} = h\nu - D_0$. For D_0 the value 1.6 eV is used [16]. The data are from several different crystals, with different initial concentrations of F_2 . Relative quantum yields measured in a given crystal are consistent within 5% error. However, absolute quantum yields, obtained from different crystals showed as much as 50% variation. The main source of errors in the determination of absolute quantum yields, is the optical scattering of the dissociating laser beam inside the 1 cm thick crystal. By using highly dilute samples (1:30000), and by optimizing the crystal growth conditions, crystals with only 10% total scattering losses could be prepared. This residual loss could be almost entirely attributed to surface reflection and surface scattering. In such crystals, the laser fluence inside the crystal is known within 5%. The main remaining source of errors are, the determination of the beam waist inside the crystal, and the assumption of gas phase absorption coefficients for

F_2 . We estimate the cumulative error on the reported absolute quantum yields to be $\approx 10\%$.

The Franck-Condon envelope of the F_2 absorption limits the longest wavelength for dissociation to 450 nm [15]. This corresponds to an excess energy of 1.16 eV. At this energy, at 12 K, the cage exit probability in Kr is measured as 12%. This is a factor of two higher than in solid Ar, where a cage exit probability of 5% was measured under identical conditions [2]. The theoretical predictions for solid Ar are also presented in fig. 3. At an excess energy of 1 eV, a probability of 55% was predicted [3]. The possible reasons for this disagreement have been previously discussed [2], and will be reiterated below.

At excess energies above 2 eV, the dissociation quantum yield measured in Kr are in agreement with the theoretical predictions for solid Ar. The experimental values in Ar are, after allowance for the larger error bars in those measurements, also in agreement with theory in this range of energies. This is a range in which cage exit probabilities are near unity. Clearly, both experiment and theory agree that the cage effect is minimal at energies above 2 eV.

The temperature dependence of quantum yields is studied at wavelengths where dissociation yields are significantly less than unity. As such we have conducted measurements at 390 nm, and 450 nm. With the present experimental method of measuring permanent dissociation probabilities, a rather narrow temperature window is available for measurements, since above ≈ 17 K, F atoms recombine in Kr [2]. This is the reason for carrying out studies at only 12 and 4 K. A clear example of the inverse temperature dependence is illustrated in fig. 4, in which the early growth of the $Kr_2^+ F^-$ exciplex emission is shown as a function of irradiation time. In this regime, which corresponds to dissociation of less than 10% of the F_2 , the growth is linear, and the relative slopes are directly related to the photodissociation rates $\Phi(T)\sigma I$. The traces, at 4.5 and 12 K, were recorded from the same spot in the crystal, under identical experimental conditions. The measurements could be repeated without observing any temperature cycling effects. Furthermore, the emission intensities were observed to be independent of temperature between 4 and 12 K, i.e. the detection quantum yield is not effected by temperature. From the linear fits to the 390 nm data, a factor of two enhancement in dis-

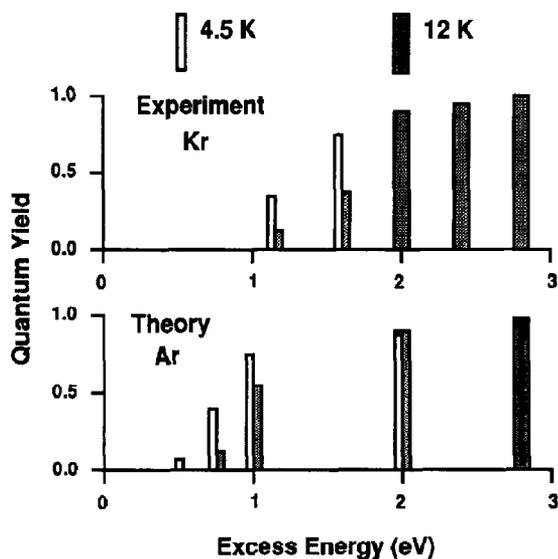


Fig. 4. Early growth of Kr_2F emission at 12 and 4.5 K. The data are from a 1 : 10000 F_2 :Kr crystal. The dissociation is carried out at 390 nm (10 mJ cm^{-2} , 10 Hz repetition rate). A weak laser operating at 277 nm is used as probe.

sociation probabilities is observed between 12 and 4.5 K, the probabilities being 38% and 75%, respectively. The absolute rate at 4.5 K was derived from a full exponential growth curve taken at 12 K. The same experiment was repeated at 450 nm, and an even stronger inverse temperature effect was observed. At this excitation wavelength, which corresponds to 1.16 eV excess energy, $\Phi(4.5 \text{ K})/\Phi(12 \text{ K}) = 3$ is observed (see table 1).

Given the picture that has emerged from the MD simulations, the similarity in energy dependence of photodissociation quantum yields in Ar and Kr is not surprising. The observation of the predicted inverse temperature dependence, makes an even stronger case for confidence in the overall model. Accordingly, one would have to accept the origin of this inverse dependence as that discovered in the simulations, namely: prealignment of the molecule along the cone of reaction in the cage, at 4 K. It is important then to wonder whether any experimental artifacts, or other considerations unaccounted in experiment or theory, could give the observed result. These considerations should also account for the possible reasons for the discrepancy between experiment and theory in absolute quantum yields at 1.16

eV. (Although, ϕ in Kr is only a factor of 4 lower than that predicted for Ar, the discrepancy in solid Ar is an order of magnitude at this energy, which is outside statistical errors in either experiment or theory.) The two obvious issues of concern are: (a) the validity of the potentials used in the simulations, (b) the experiments monitor permanent dissociation, while the theory tracks dissociation on a time scale typically shorter than 50 ps. These are respectively discussed below.

The effect of potentials has not yet been systematically explored. Based on the qualitative agreement between experiment and theory, we may conclude that the chosen potentials reproduce the gross dynamics. However, when making absolute quantitative comparisons, especially near the threshold energies for dissociation, details may become important. Here, the choice of the rare gas-halogen (Rg-X and Rg- X_2) potentials are in question. To date, the gas phase Rg-X ($^2\Sigma_{1/2}$) potential has been used, with the assumption of pairwise additivity [3,7,9]. The ground state interactions of $\text{F}(^2\text{P}_{3/2})$ with $\text{Ar}(^1\text{S}_0)$ give rise to the closely spaced pair potentials $\text{X}(^2\Sigma_{1/2})$ and $\text{A}(^2\Pi_{1/2})$ in the $\text{C}_{\infty v}$ point group of the isolated pair [11]. For an F atom packed in a crystalline solid of cubic symmetry, these states should mix, and give rise to a highly degenerate set of surfaces. The pairwise summation of only one of these diatomic potentials over all neighbors, cannot yield the full representation of the effective interaction potential. Given the more repulsive nature of the Rg-X(A) surface, we suspect that its incorporation in the theoretical treatments would result in a reduction in observed cage exit probabilities. The extent to which the theoretical yields would be modified by such considerations, is not known at present. Clearly, the next generation of simulations will have to address this issue more rigorously. With respect to the inverse temperature dependence of dissociation probabilities, the choice of potentials is not strictly a quantitative issue. The inverse temperature dependence in the simulations arise from a subtle effect, namely, the fact that at 4 K F_2 freezes in a librational well, while at 12 K it rotates eccentrically in the substitutional Ar trap. This dynamics is sensitive to the F_2 -Rg potentials, which in the simulations is obtained from a pairwise sum of F-Rg potentials. Therefore, the simulated interaction is

necessarily more anisotropic than the true molecule-atom potential. At present, there is no independent experimental input to check this predissociation dynamics.

Although, we have previously verified that geminate recombination does not occur outside the photodissociation pulse width of ≈ 20 ns [1]; the lower quantum yields measured experimentally could in principle be rationalized as due to recombination occurring in the time window of 50 ps–20 ns. This is a time window in which neither experiment nor theory has a direct input. Geminate recombination within the laser pulse would result in the observation of lower cage exit probabilities in the experiment. This consideration is evidently of no concern at high excess energies, where unit quantum yields are observed in both experiment and theory. At low excess energies, if indeed significant recombination were to occur, and the probability of recombination were higher at 12 K than at 4 K, we would then effectively observe higher permanent dissociation probabilities at the lower temperatures. The main arguments against this interpretation have to do with the lessons learned from the molecular dynamics simulations. The simulations are propagated in time until all atoms are thermalized, this usually occurs on the time scale of ≈ 10 ps. All recombination during this time period is taken into account in the final count of dissociation probabilities, and indeed geminate recombination after cage exit of fragments is observed in many trajectories [3]. Once the system is thermalized, no further recombination is observed for time scales of order ≈ 50 ps. Since no provisions are made for dissipation of energy outside the simulated cell, thermalization occurs at abnormally high temperatures. As an example, for a dissociation excess energy of 1.5 eV, when 173 mobile atoms are included in the simulation cell, the final temperature of the assembly will be ≈ 80 K. Yet no recombination is observed. In a real system, rapid dissipation of energy into the solid bulk is to be expected, reducing the likelihood of any further recombination. We, therefore, do not believe that recombination could explain the observed inverse temperature dependence.

4. Conclusions

We have shown that the photodissociation dynamics of F_2 in solid Kr is similar to that in solid Ar, and in qualitative agreement with the general features of the MD simulations of that system. Although, in the time window of 50 ps–20 ns neither experiment nor theory have a direct input, we believe that the measured permanent dissociation probabilities correspond to the quantum yields calculated in the simulations. As such, we conclude that the observed inverse temperature dependence of F_2 photodissociation quantum yields in Kr, are due to prealignment of the molecule along the reaction cone, as observed in the MD simulations of F_2 in Ar.

There clearly is a need for creating a more direct overlap between experiment and theory. Measurements on picosecond time scales are the most direct means for accomplishing this goal. There also is a need for iteration between experiment and theory, in order to account for quantitative differences between the two.

Acknowledgement

This research was funded by the United States Air Force Astronautics Laboratory, under contract F04611-87-K-0024. A Grant from the Academy of Finland to HK, during his stay at Irvine, is gratefully acknowledged.

References

- [1] H. Kunttu, J. Feld, R. Alimi, A. Becker and V.A. Apkarian, *J. Chem. Phys.*, in press.
- [2] J. Feld, H. Kunttu and V.A. Apkarian, *J. Chem. Phys.*, in press.
- [3] R. Alimi, R.B. Gerber and V.A. Apkarian, *J. Chem. Phys.* 92 (1990) 3551.
- [4] V.E. Bondybey and C. Fletcher, *J. Chem. Phys.* 64 (1976) 3615.
- [5] V.E. Bondybey and L.E. Brus, *J. Chem. Phys.* 64 (1976) 3724; 65 (1971) 71.
- [6] N. Schwentner and V.A. Apkarian, *Chem. Phys. Letters* 154 (1989) 413.
- [7] R. Alimi, R.B. Gerber and V.A. Apkarian, *J. Chem. Phys.* 89 (1988) 174.

- [8] R. Schrieffer, M. Chergui, H. Kung, V. Stepanenko and N. Schwentner, *J. Chem. Phys.* 91 (1989) 4128;
R. Schrieffer, M. Chergui, Ö. Ünal, N. Schwentner and V. Stepanenko, *J. Chem. Phys.*, submitted for publication.
- [9] R. Alimi, A. Brokman and R.B. Gerber, *J. Chem. Phys.* 91 (1989) 1611.
- [10] H. Friedman and S. Kimel, *J. Chem. Phys.* 43 (1965) 3925.
- [11] C.H. Becker, P. Casavecchia and Y.T. Lee, *J. Chem. Phys.* 70 (1979) 2986.
- [12] W. Rudnick, R. Haensel, H. Nahme and N. Schwentner, *Phys. Stat. Sol.* 87(a) (1985) 319.
- [13] W. Lawrence and V.A. Apkarian, J.G.R. -Atmospheres, in press: *Israel J. Chem.* 30 (1990), in press.
- [14] M.E. Fajardo, R. Withnall, J. Feld, F. Okada, W. Lawrence, L. Wiedeman and V.A. Apkarian, *Laser Chem.* 9 (1988) 1.
- [15] R.B. Steunenberg and R.C. Vogel, *J. Am. Chem. Soc.* 78 (1956) 901.
- [16] E.A. Colbourn, M. Dagenais, A. Douglas and J.W. Raymonds, *Can. J. Phys.* 54 (1976) 1343.